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Investigations on LPG sensing of nanostructured zinc oxide synthesized via mechanochemical method

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***Abstract:* -** Present paper reports synthesis of zinc oxide and its application as liquefied petroleum gas sensor. The structural and morphological characterizations of the sample were analyzed by X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The average value of crystallite size of ZnO calculated from Scherrer's formula is found to be 50 nm. SEM images exhibit the porous nature of sensing material with a number of active sites. The LPG sensing properties of the zinc oxide were investigated at room temperature for different vol.% of LPG. The variations in electrical resistance were measured with the exposure of LPG as a function of time. The maximum value of sensitivity was found to be 12.3 for 4 vol. % of LPG. These experimental results show that nanostructured zinc oxide is a promising material for LPG sensor.

***Keywords*: -** *Sensor, morphology, sensitivity, nanomaterial, LPG*

I. INTRODUCTION

Zinc oxide due to the large band gap 3.37 eV and high exciton binding energy of 60 meV shows various useful properties and gives large and diverse range of growth of different type of morphologies such as nanosheets, nanocombs, nanobelts, nanowires and nanorings, which may be used in various applications [1-3]. It is one of the promising materials among metal oxides for use in humidity sensors [4-9] and gas sensors [10-17]. Basic requirement for the sensor is its change in electrical conductivity with exposure of LPG to semiconducting oxides which depends on their band gaps, surface morphology, size, diffusion rate of gas and specific surface area [18]. The semi-conductive properties of metal oxides represent the basis for their use as gas sensors, since the number of free charge carriers within the metal oxide and thus its electrical conductivity reversibly depends on the interactions with the ambient gas atmosphere [19]. For sensor application of nanostructured materials the charge transfer either results from adsorption or chemisorptions of gas molecules at the sensor surface, or from diffusion of the gas into the bulk of the sensor material [20].

The sensing mechanism of the reducing gases consists in the change of the electrical resistance resulting from chemical reaction between the gas molecule and adsorbed oxygen on the metal oxide surface [21-22]. As the sensing phenomenon mainly takes place on the surface of sensing element, the surface morphology has an essential role on the sensitivity of sensor. Also, the sensitivity of the sensor depends on the method used for production of nanoparticles. The efficiency of the chemical sensor increases as particle size decreases [23].

II. EXPERIMENTAL

2.1 Synthesis of material

ZnO is prepared by chemical precipitation method using zinc sulphate and sodium hydroxide. For the preparation of zinc hydroxide, sodium hydroxide solution was mixed drop wise to zinc sulphate and stirred for 1 h. Also some drops of poly ethylene glycol-400 (PEG-400) was added, which works as capping agent and prevents the grain growth. After that the solution is sonicated for 30 minutes using ultrasonic machine. The obtain hydroxides were dried in an electrical oven at 100°C for 8-10 h. In addition, the powder was annealed at 400°C for 2 h, resulting in complete crystallization into powder. The pellet having thickness 4 mm and diameter 10 mm was prepared by using hydraulic pressing machine under pressure 616 MPa at room temperature.

2.2 Characterizations of n-type ZnO

2.2.1 Scanning Electron Microscopy (SEM)

The surface morphology of the synthesized powder in form of the pellet was analyzed using a scanning electron microscope (SEM, LEO-Cambridge) as shown in Fig. 1. SEM images show porous nature of the prepared pellet with clusters of crystallites over the entire surface of the material. The porosity of the material is an imperative parameter regarding gas sensing point of view as the pellet has a number of active sites.

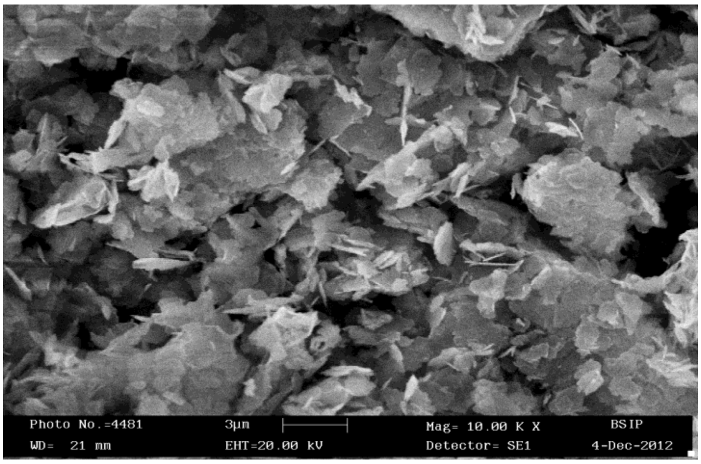

FIGURE 1 Scanning electron micrographs of ZnO pellet.

2.2.3 X-Ray Diffraction

The crystal structure and phase identification of material was analyzed using X-ray Diffractometer (X-Pert, PRO PANalytical XRD system, Nether land) with Cu K_α radiations as source having wavelength 1.5418 Å. X-Ray diffraction pattern show extent of crystallization of the sample. The average crystallite size (*D*) of the sensing material can be calculated by the Debye-Scherrer's formula, which is given by

$$D = K\lambda / \beta\cos\theta$$

where K= 0.94 is Scherrer's coefficient, which depends on the shape of the crystallite and the type of defects present, λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the angle of diffraction. Fig. 2 show XRD patterns of the zinc oxide prepared recorded for 2θ = 30° to 90° reveal that the sensing material consists of larger peaks of ZnO. The average value of crystallite size of ZnO calculated from Scherrer's formula is found to be 50 nm corresponding to plane (101) having full width half maxima (FWHM) values of 2.460°.

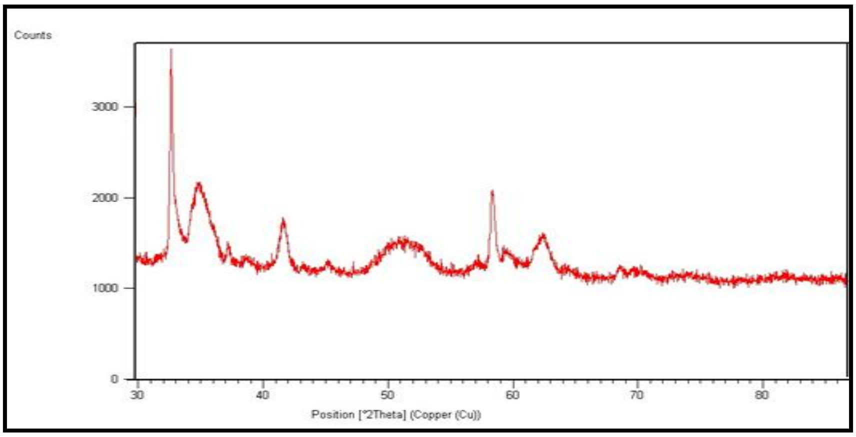

FIGURE 2 X-Ray Diffraction of ZnO powder prepared at room temperature

2.3 Gas Sensing Measurements

Prima facie before the exposition of LPG to the sensing element, the gas chamber was allowed to evacuate at room temperature for 15–20 min and the stabilized resistance was taken as Ra. For the LPG sensing measurements a special gas chamber was designed which consists of a gas inlet and an outlet knob for LPG exclusion. The schematic diagram of LPG sensing set-up is shown in Figure 3. The sensing pellet was inserted between the two Ag electrodes inside the glass chamber having two knobs. One knob is associated with the concentration measuring system (gas inlet) and other is an outlet knob for releasing of the gas. Now this was exposed with LPG and variations in resistance with the time for different vol % of LPG were recorded by using Keithley electrometer (Model: 6514).

Sensitivity of the LPG sensor is defined as the change in resistance in the presence of gas (R_g) to the resistance in presence of air (R_a) that is

$$S = R_g / R_a$$

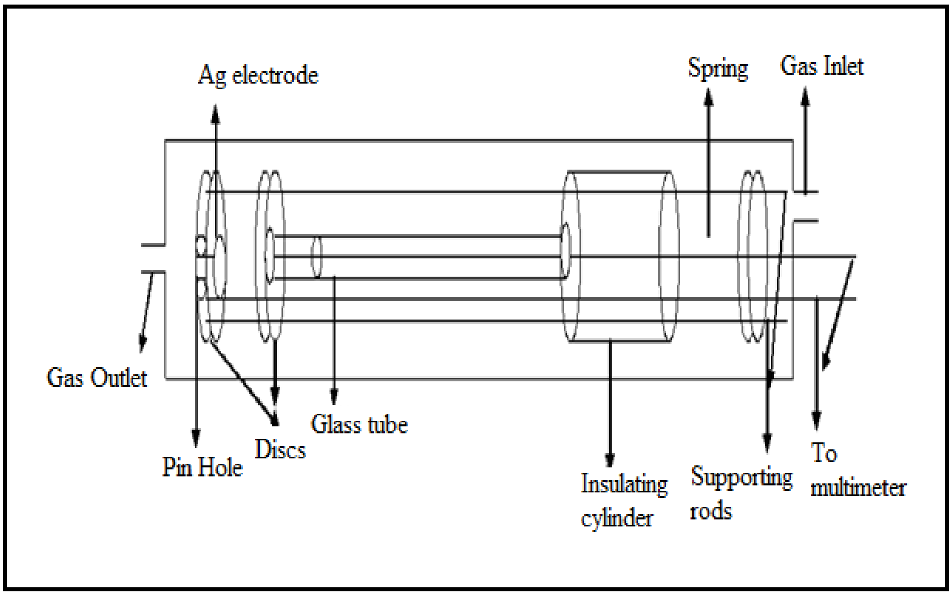

FIGURE 3 Experimental-set-up

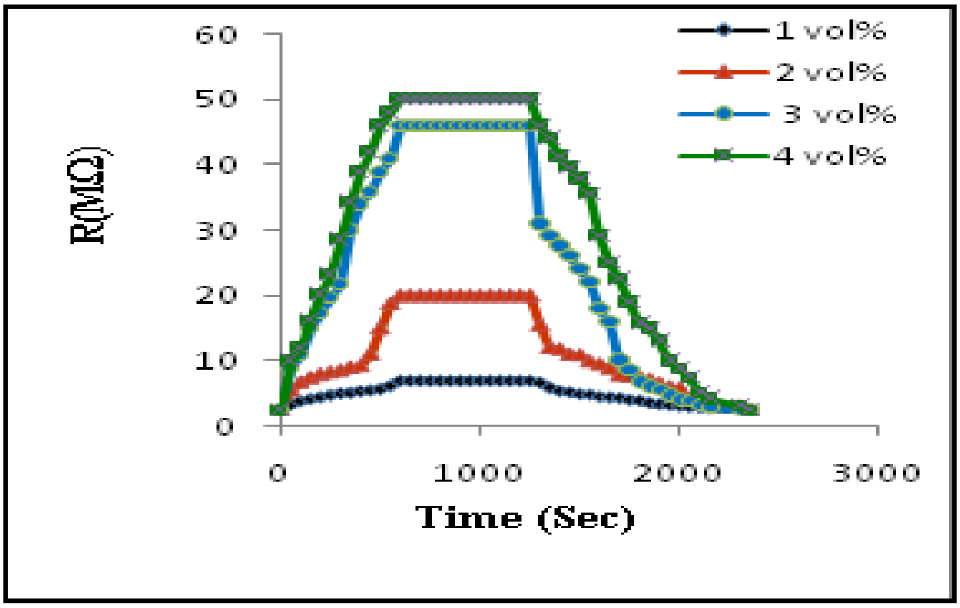

FIGURE 4 Variations in resistance of pellet with time after exposure for different vol% of LPG

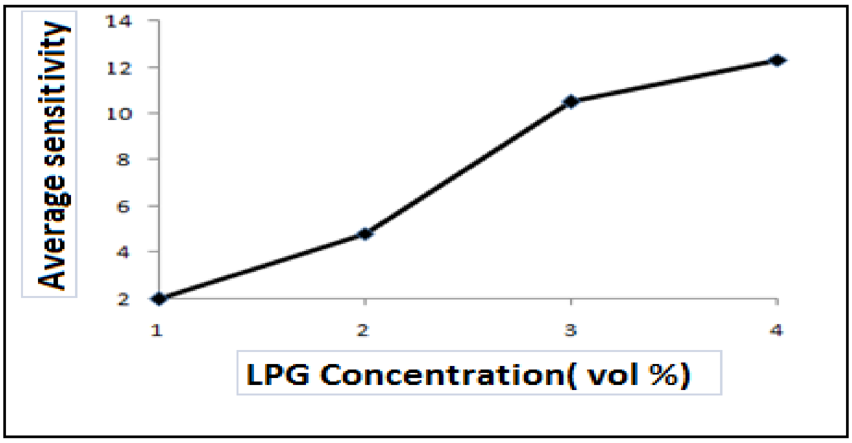

FIGURE 5 Variations of average sensitivity with different concentrations of LPG

Fig. 4 illustrates the variations in resistance of the pellet with time after exposure for different vol.% of LPG at room temperature. Curves for 1 and 2 vol% of LPG show small variation in resistance with time after exposure. Curve for 3 vol% of LPG exhibits improved response and has better sensitivity than 1 and 2 vol% of LPG. Further, for 4 vol% of LPG resistance increases sharply with time after exposure up to 600 s and then become constant.

Fig. 5 exhibits the variations of average sensitivity with different concentrations of LPG and it was found that as the concentration of LPG (in vol.%) increases, the average sensitivity of sensor increases linearly upto 3 vol% of LPG later it increases slowly. The linear increment of the sensitivity of the sensor is a significant factor for device fabrication. The maximum sensitivity was obtained for 4 vol% of LPG and is ~ 12.3.

The gas sensing mechanism of zinc oxide based LPG sensor is a surface controlled phenomenon i.e., it is based on the surface area of the pellet at which the LPG molecules adsorb and reacts with pre-adsorbed oxygen molecules. As mentioned earlier, the pellet is porous. Therefore, the oxygen chemisorptions centers viz., oxygen vacancies, localized donor and acceptor states and other defects are formed on the surface during synthesis. These centers are filled by adsorbing oxygen from air. After some time equilibrium state is achieved between oxygen of zinc oxide and atmospheric oxygen through the chemisorptions process at room temperature. The stabilized resistance at present state is known as resistance in presence of air (R_a). The pellet interacts with oxygen by transferring the electrons from the conduction band to adsorbed oxygen atoms, resulting into the formation of ionic species such as O_2 , O_2^- , O^- or O^{2-} . The reaction kinematics may be explained by the following reactions:

$$O_2(gas) \leftrightarrow O_2(ads)$$
$$O_2(ads) + e^- \longrightarrow O_2^-$$

The electron transfer from the conduction band to the chemisorbed oxygen results in the decrease in the electron concentration at surface of the pellet. As a consequence, an increase in the resistance of the pellet is observed. The conduction process in gas sensing is electronic and the chemisorptions of atmospheric gases take place only at the surface of the zinc oxide. The overall conduction in a sensing element, which will monitor the sensor resistance, is determined by the surface reactions resulting out from the charge transfer processes with the sensing element. In LPG molecules the reducing hydrogen species are bound to carbon, therefore, LPG dissociates less easily into the reactive reducing components on the pellet surface. When the pellet is exposed to reducing gas like LPG, the LPG reacts with the chemisorbed oxygen and is adsorbed on the surface of pellet then the exchange of electrons between the LPG and oxide surface upon adsorption would be taken place, i.e., a surface charge layer will be formed. When the LPG reacts with the surface oxygen ions then the combustion products such as water depart and a potential barrier to charge transport would be developed i.e., this mechanism involves the displacement of adsorbed oxygen species by formation of water. The overall reaction of LPG with the chemisorbed oxygen may be taken place as shown below:

$$2C_nH_{2n+2} + 2O_2^- \longrightarrow 2C_nH_{2n}O + 2H_2O + 2e^-$$

Where C_nH_{2n+2} represents the various hydrocarbons. These liberated electrons recombine with the majority carriers (holes) of sensing pellet resulting in a decrease in conductivity. The formation of barrier is due to reduction in the concentration of conduction carriers and thereby, results in an increase in resistance of the sensing element with time. As the pressure of the gas inside the chamber increases, the rate of the formation of such product increases and potential barrier to charge transport becomes strong which has stopped the further formation of water constituting the resistance constant. The free charge carriers have to overcome the surface barriers appearing at the surface of the grains.

It was observed that as the concentration of LPG increases, the average sensitivity increases linearly in the beginning and later it becomes saturated. The linear relationship between sensitivity and gas concentration may be attributed to the availability of sufficient number of sensing sites on the pellet to act upon the LPG. The low concentration implies a lower surface coverage of gas molecules, resulting in a lower surface reaction between the surface adsorbed oxygen species and the gas molecules. The increase in LPG concentration increases the surface reaction due to a large surface coverage. Further increase in the LPG concentration does not increase the surface reaction and eventually saturation takes place. Thus, the maximum sensitivity was obtained at higher concentration of LPG i.e. 4 vol.%. The linearity of average sensitivity for the LPG (< 3 vol.%) suggests that the zinc oxide pellet can be reliably used to monitor the LPG over this range of concentration. As the lower explosive limit (LEL) for LPG is 4.0 vol. % [24] therefore, response is measured up to 4.0 vol. % in order to detect the LPG below LEL for safety requirement. Figure 6 shows the reproducibility curve of sensor after two month. It was found that after two month, it performs 90% of its initial performance.

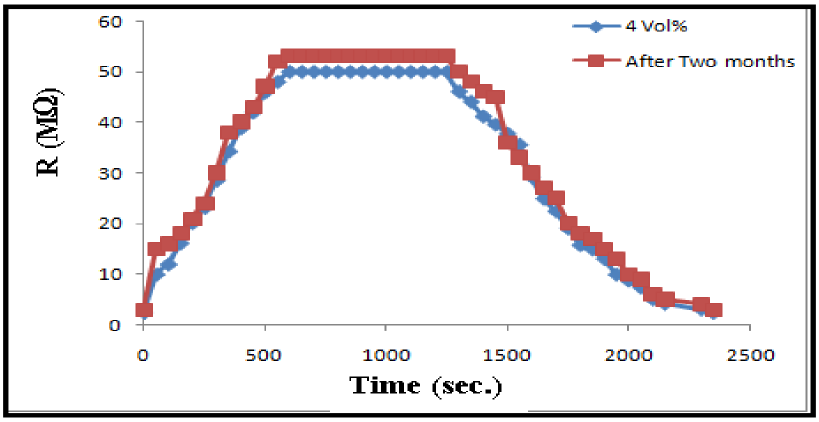

Figure 6 Reproducibility curve of sensor after two months

III. CONCLUSION

We have successfully synthesized nanostructured Zinc oxide via mechanochemical method. It was found that synthesized zinc oxide works as a good LPG sensor at room temperature and average sensitivity of this sensor is found 12.3 for 4 vol % LPG. As detection of Liquefied petroleum gas is very important for disaster management purpose that's why this study is quite appreciable for commercial applications. Good sensitivity, reproducibility and stability demonstrate the promise of this sensor for LPG determination in the industrial and environment monitoring. Thus, this study demonstrates the possibility of utilizing zinc oxide pellet as a sensing element for the detection of LPG.

IV. ACKNOWLEDGEMENT

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